

Copper(II) adsorption by activated carbons from pecan shells: Effect of oxygen level during activation

K. Thomas Klasson*, Lynda H. Wartelle, James E. Rodgers III, Isabel M. Lima

U.S. Department of Agriculture, Agricultural Research Service, Southern Regional Research Center, 1100 Robert E. Lee Blvd., New Orleans, LA 70124, USA

ARTICLE INFO

Article history:

Received 17 September 2008

Received in revised form 31 October 2008

Accepted 25 January 2009

Keywords:

Activated carbon
Agricultural by-products
Phosphoric acid activation
Pecan shells
Oxidation

ABSTRACT

Agricultural by-products represent a considerable quantity of harvested commodity crops. The use of by-products as precursors for the production of widely used adsorbents, such as activated carbons, may impart a value-added component of the overall biomass harvested. Our objective in this paper is to show how the partial oxidation of phosphoric acid-impregnated pecan shells resulted in activated carbons with different affinities for a typical metal ion, copper(II), in aqueous sorption studies. The oxygen level was varied during activation by altering the sweep gas (air) flow rate in the furnace. Surface area and micropore volume of the produced carbon did not vary significantly with degree of oxidation, while the surface charge and the adsorption capacity were strongly dependent on the oxidative conditions. Surface area functional groups of C=O, aromatics, and phosphorus were confirmed by infrared spectroscopy. The results show that the yield of activated carbon product was higher in the more oxygen-deprived atmosphere but that the product had a lower affinity for adsorbing copper from an aqueous solution. The carbon with the highest adsorptive capacity was produced by activation in approximately 14% oxygen atmosphere, yielding adsorption values of 0.97 and 1.3 mmol of copper(II) per gram of carbon when the carbon had been in contact with a copper(II) solution with initial concentration of 10 and 20 mM of copper, respectively.

Published by Elsevier B.V.

1. Introduction

A variety of resources may be considered for activated carbon generation: coal, wood char, and agricultural by-products. Unlike coal, wood and agricultural by-products are abundant, low cost and renewable. In a recent report, it was estimated that 129 and 176 million dry metric tons are available for bioenergy and bio-products from forestry and agriculture, respectively; and this could be increased substantially with different agricultural management practices (USDOE, 2005).

The quantity of tree nut shells as raw material for activated carbons production, or other uses, is significant. Tree nut production in 2006 was 1.6 million tons in the U.S. and had a value of \$3.45 billion, with almond, walnut, pistachio, and pecan representing the most popular nuts (NASS, 2007). Pecans are grown in 15 states in the U.S. and, even though they may be marketed and sold with shells, the majority of pecans are sold without shell. In 2006, 84,000 tons of pecans were shelled, resulting in an estimated 46,000 tons of shells as a by-product.

Activated carbons are not commonly marketed for their ability to adsorb metal cations from solutions; more often they are sold for their ability to remove organics, dyes, and chlorine. The method of activation is often steam, resulting in a porous activated carbon with high surface area. While steam activation is the most common, acid activation with hydrochloric acid was investigated as early as 1938 (Whitehead and Warshaw, 1938) to produce carbon for dye removal. Chemical activation with phosphoric acid, zinc chloride, or carbonate salts was used for activation of almond shells (Bevia et al., 1984) under a nitrogen atmosphere and the resulting carbons were characterized for adsorption of organics. Acid activation of carbons made from wood and coal under a nitrogen atmosphere was investigated by Jagtoyen et al. (1992) and Jagtoyen and Derbyshire (1993) but no attempt was made to investigate cationic metal uptake. Jagtoyen et al. (1992) and Jagtoyen and Derbyshire (1993) concluded that the phosphoric acid, when applied at low temperatures (450 °C), promotes dehydrogenation, cross-linking, sulfur removal, and increased aromatization in the resulting activated carbon product. Introduction of air during phosphoric acid activation was proposed by Molina-Sabio et al. (1995a) as a process simplification effort. That work determined that air was not detrimental to yield or micropore volume, when sufficient phosphoric acid was used for impregnation. The authors also found that the bulk density of these carbons tended to be higher than

* Corresponding author. Tel.: +1 504 2864511; fax: +1 504 2864367.

E-mail address: Thomas.Klasson@ars.usda.gov (K.T. Klasson).

those produced under a nitrogen atmosphere, and it was speculated that additional oxygen was chemisorbed onto the carbons, generating a denser activated carbon. Cation adsorption was not part of the study. A patent was granted to Toles et al. (2000a), who demonstrated that phosphoric acid activation in an air atmosphere produced activated carbons from a variety of nut shells that had superior adsorptive capacity for metal cations. Various combination of nitrogen, air, rapid cooling, and activation temperatures during phosphoric acid activation was also studied by Toles et al. (1998, 2000b). It was found that pecan and almond shells pyrolyzed and activated at 450 °C for 1 h with an air atmosphere produced activated carbons with high surface area (1138–1458 m²/g) and significant adsorptive capacity for copper(II) ions. A slightly more complex method of activation at 170 °C and 450 °C, with an air atmosphere produced activated carbons with less surface area but with better copper ion adsorptive capacity. It was determined that the oxidation of the carbon surface was important as it produced a negative surface charge, which contributed to its ability to adsorb cations, and a linear relationship between surface charge and metal adsorptive capacity has already been demonstrated by Toles et al. (1998) and Lima et al. (2004). The process was further evaluated and the predicted cost of producing phosphoric acid activated carbons from pecan shells was estimated at \$2.89/kg (Ng et al., 2003).

Since past research has shown that the gas composition during activation of phosphoric acid impregnated material is important, we initiated a set of experiments to produce activated carbons via phosphoric acid activation of pecan shells under different oxidative conditions. This was accomplished by altering the flow of gas (to achieve different oxygen levels) during pyrolysis and activation. The carbons were then characterized and evaluated for their ability to adsorb cations.

2. Methods

2.1. Materials

Pecan shells were obtained from H.J. Bergeron Pecan Shelling (Boyce, LA). Extraneous matter was removed, and the shells were ground in a cutting mill (Type SM2000; Retsch GmbH, Haan, Germany) and sieved to retain the 0.84–2 mm (nos. 10–20 sieve) fraction for conversion to activated carbon. The size fraction was selected based on previous experiments (Toles et al., 1998; Lima et al., 2004; Marshall et al., 2007).

A commercial carbon, Norit C, from Norit Americas, Inc. (Marshall, TX) was used for comparison purposes. This carbon was chosen because it is made via a similar activation strategy as the one used here. Based on manufacturer's information, Norit C is a phosphoric acid-activated carbon used for adsorbing high molecular organics.

2.2. Experimental methods

The phosphoric acid activation of the pecan shells was performed using the same method previously done with flax shive (Marshall et al., 2007). To summarize: 100 g shells and 100 g phosphoric acid (30% by weight) were mixed in a porcelain evaporating dish and the material was allowed to absorb the phosphoric acid solution overnight. Activation was then performed by placing the dish in a furnace with retort (Lindberg, Type 51662-HR, Watertown, WI) for 4 h at 450 °C with either 100, 400, 600, 1200, 1600, or 2000 mL/min of air flow. The void volume of the furnace was approximately 22 L and the heating rate was approximately 12 °C/min (independent of air flow rate.) The off-gas composition from the furnace was monitored during the heating and activation

process. After activation, the furnace (and carbon) was allowed to cool overnight with constant air flow. The air flow during heating, activation, and cooling was kept constant during runs. The resulting carbon was washed five times in hot water (90 °C) at a ratio of approximately 100:1 (w/w, water:carbon) and only the fraction above no. 60 sieve screen (i.e., >0.25 mm) was retained. While the commercial carbon (Norit C) was not activated, it was found to contain residual phosphoric acid and was washed in the same manner as the experimental carbons. The carbons were oven-dried at 80 °C overnight.

The carbons were physically and chemically characterized for nitrogen gas adsorption, surface charge, and possible chemically active surface groups using a variety of methods described in Section 2.3.

Two-point adsorption studies were carried out in covered 50-mL glass beakers using 0.25 g of activated carbon and 25 mL of aqueous solution. This solution contained 10 or 20 mM of copper(II) chloride and was buffered at pH 4.8 with 20 mM acetic acid and 30 mM sodium acetate. The solution and activated carbon were stirred (using a magnetic stirrer bar) at approximately 300 rpm for 24 h. After contact, the solution was diluted before metals analysis. The concentration after adsorption was compared to that of a control solution containing no activated carbon but which had undergone all the other experimental procedures. The adsorption experiments were run in duplicate. Similar adsorption studies have previously been reported (Toles et al., 1998; Lima et al., 2004; Marshall et al., 2007), which allowed for easy comparison of results.

2.3. Analytical methods

The composition of the off-gas from the furnace during heat-up and activation was analyzed with an Enerac 500 Emissions Analyzer (Enerac, Westbury, NY) attached to a computer. This analyzer pulls gas through a particle filter and into a chamber equipped with a set of electro-chemical sensors for oxygen, combustibles, carbon monoxide, and sulfur dioxide. Carbon dioxide is determined through calculations from oxygen and carbon monoxide levels.

Surface areas for the activated carbons were determined from nitrogen gas adsorption isotherms at −196 °C using a Nova 2000 Surface analyzer (Quantachrome Instruments, Boynton Beach, FL) that reports Brunauer–Emmett–Teller (BET) surface area and micropore volume measurements. The carbons were conditioned under vacuum at 200 °C before nitrogen adsorption.

Surface charge was determined (in duplicates) at pH 5 by a procedure previously described (Lima et al., 2004). The approach involves contacting a sample of activated carbon (H⁺-saturated at pH 5) with a known volume of 0.1 M NaOH. The base solution is then titrated using an HCl solution, yielding a value for the amount of base neutralized by the protonated carbons surface (in mmol H⁺/g).

The raw material and the activated carbons were subjected to Fourier transform infrared (FTIR) spectra analysis using a Bruker Optics Tensor 27 FTIR spectrometer (Bruker Optics, Billerica, MA) with a Zn–Se attenuated total reflectance (ATR) crystal. Sixty-four (64) scans were made of each sample at 4 cm^{−1} resolution from 4000 cm^{−1} to 600 cm^{−1}.

After completion of copper(II) ion adsorption experiments, liquid samples were removed and filtered using a disposable syringe with a 0.22-μm-pore-size Millipore filter (Millipore Corp., Bedford, MA). The filtered sample was diluted a 100-fold with 4 vol.% nitric acid (Ultrapure, ICP grade) and analyzed using an Inductively Coupled Plasma Optical Emissions Spectrometer (Profile Plus, Teledyne/Leeman Labs, Hudson, NH).

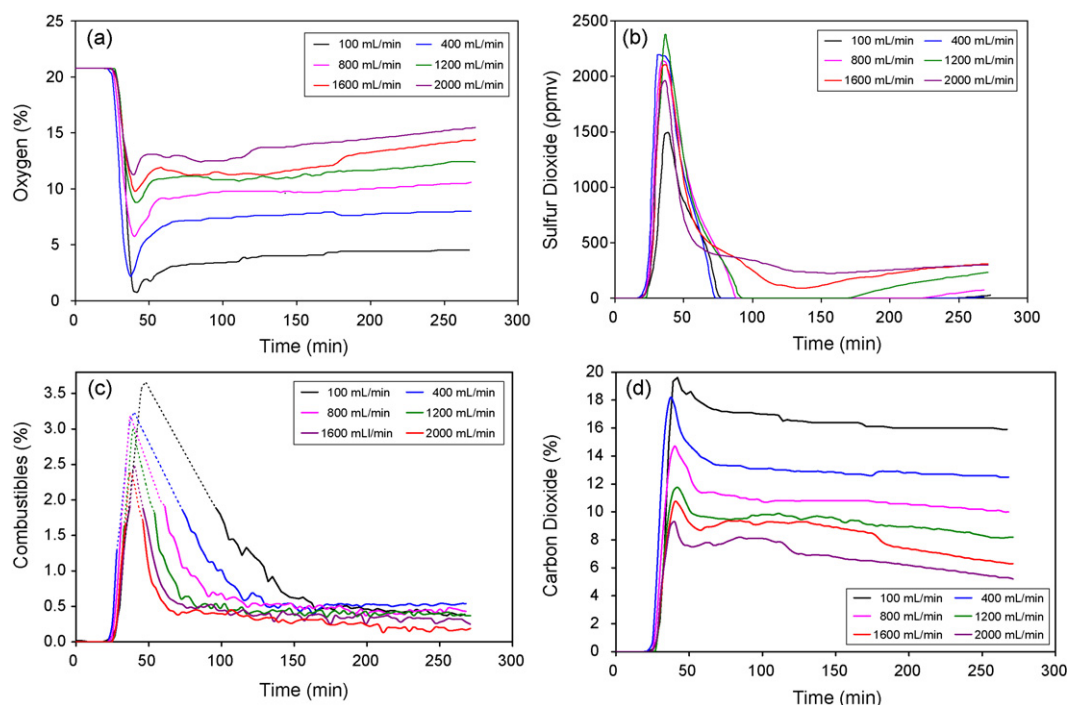


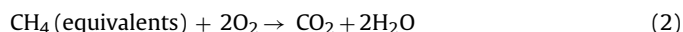
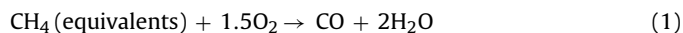
Fig. 1. (a–d) Oxygen, sulfur dioxide, combustibles (as methane equivalent), and carbon dioxide (calculated) concentration profiles for different activation air flow rates as a function of time of pyrolysis/activation of phosphoric acid impregnated pecan shells. The dashed part of the curves in (c) represents estimated values outside the range of the analytical instrument. They were estimated by using the trend of the existing data, as it approached the upper limit of the instrument.

3. Results and discussion

3.1. Off-gas composition during pyrolysis and activation

The composition of the off-gases from the furnace is shown in Fig. 1(a)–(d) for the different activation air flow rates. As is noted in Fig. 1(a), the oxygen content in the off-gas (and thus in the furnace) was dependent on the activation air flow rate. There was an initial dip in the oxygen level, followed by a gradual increase over time. The nominal oxygen concentration for the latter part of the treatment is listed in Table 1. It can be concluded that there is a net consumption of oxygen during the pyrolysis/activation cycle. In the present studies conducted in an oxygen-rich atmosphere, it was not surprising that sulfur dioxide was present in the off-gas (Fig. 1(b)). Sulfur loss during acid activation was noted by Jagtoyen et al. (1992) when coal was activated in a nitrogen atmosphere; in this case hydrogen sulfide was released, while other sulfur gases were absent. Here we show that the oxidized form of sulfur is released in an oxidizing atmosphere. The evolution of combustible gases was noted and, as shown in Fig. 1(c), their sharp rise corresponded to the noted decrease in oxygen (Fig. 1(a)); however, it is clear that the decrease in oxygen cannot be explained by simply the dilution of the gas with the gases volatilized from the pecans. Oxygen possibly reacts with the carbon contained in the shells and the volatile (combustible)

gases generated from the heating of the materials. The reaction of a combustible gas (as methane equivalents) with oxygen to create carbon monoxide and carbon dioxide is shown in Eqs. (1) and (2):



While oxygen also reacts with sulfur to produce sulfur dioxide (see Fig. 1(b)), the amount of oxygen used for this reaction is small. The instrument-calculated concentration of carbon dioxide is shown in Fig. 1(d). Carbon monoxide was also recorded by the instrument; however, the level in the exhaust exceeded the maximum limit of 1900 ppmv for the duration of the activation cycle.

3.2. Surface analysis and oxidation of activated carbon surface

The surface charge correlated well with the nominal oxygen level in the furnace indicating that a higher oxygen level resulted in more groups on the carbons surface capable of adsorbing positive ions (H^+ equivalents) (see Fig. 2). The ability for the activated carbons to adsorb copper(II) was strongly dependent on the surface charge, which was in agreement with studies using other activation strategies (Toles et al., 1998, 1999; Wartelle and Marshall, 2001; Lima et al., 2004).

Table 1
Carbon activation properties for experimental and commercial carbons.

Carbon	Activation air flow rate (mL/min)	Nominal oxygen level ^a (%)	Surface area (m ² /g)	Micropore volume (mL/g)
I	100	4.0	904	0.329
II	400	7.6	895	0.326
III	800	9.9	864	0.316
IV	1200	11.4	885	0.325
V	1600	12.5	867	0.319
VI	2000	14.0	915	0.334
Norit C	NA	NA	1237	0.530

^aThe nominal oxygen level was calculated as an average oxygen concentration in the furnace off-gas between 60 and 270 min (see Fig. 1(a)).

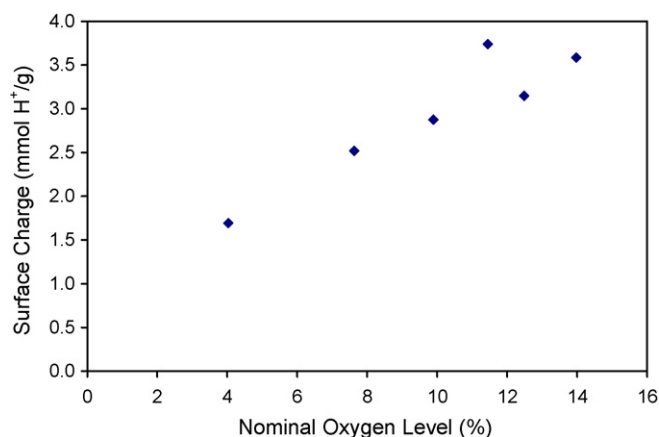


Fig. 2. Surface charge for activated carbons made under different oxidative conditions.

The ATR FTIR spectra for pecan shells and phosphoric acid-activated carbon samples at different activation oxygen levels are shown in Fig. 3. Major spectral changes are readily observed with the reaction of the pecan shells and phosphoric acid, and these changes are observed even at the low activation oxygen levels (low air flow rates). The FTIR spectral results for these activated carbon samples are in good agreement with those obtained by previous studies on activated carbons (Guo and Rockstraw, 2007; Jagtoyen et al., 1992; Solum et al., 1995). The aliphatic C–H stretching bands present in the pecan shell at 2960, 2924, and 2854 cm^{−1} are significantly minimized, indicating a loss of aliphatic nature with the reaction of phosphoric acid, air, and heat; which is similar to results obtained for phosphoric acid-activation of coal (Jagtoyen et al., 1992). The absorption band around 1700 cm^{−1} can be assigned to C=O stretch in carboxylic acids, ketones, aldehydes, lactones, or esters (Guo and Rockstraw, 2007), and the increase and slight shift of the peak at 1704 cm^{−1} during activation can be possibly attributed to changes of esters and carboxyl groups in favor of ketones and aldehydes (Solum et al., 1995). These types of groups have previously been noted with a selective titratable surface charge technique with cationic selective activated carbons (Toles et al., 1999). The absorption at 1612 cm^{−1} in the pecan shells decreased, but a new peak was observed for the activated carbon samples at 1560 cm^{−1}, indicating a shift in an absorption that has been assigned to condensation of aromatic rings or C=C (Jagtoyen et al., 1992). The general increase in band intensities with activation treatment from around 1300 to 600 cm^{−1} is indicative of

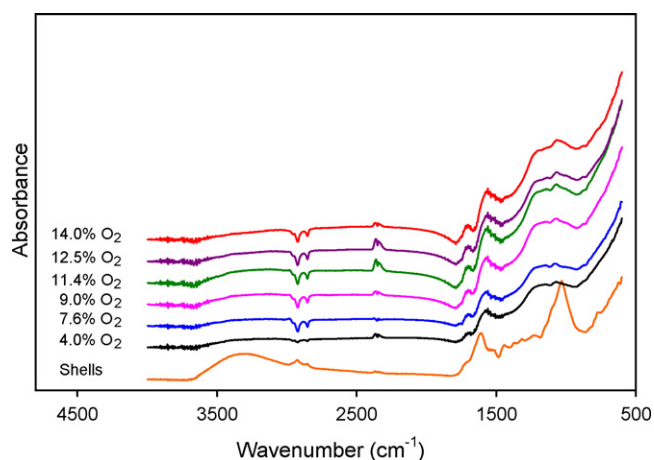


Fig. 3. FTIR spectra; stacked, 4000–600 cm^{−1}; of ground pecan shells and phosphoric acid activated carbons made under different oxidative conditions.

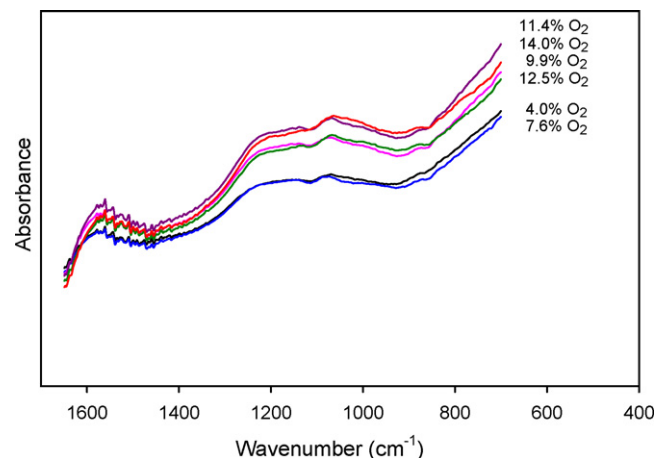


Fig. 4. FTIR spectra; overlapped, 1650–700 cm^{−1}; of ground pecan shells and phosphoric acid activated carbons made under different oxidative conditions.

phosphorous-containing groups being formed during heat treatment, as noted prominently by the absorption peaks formed with activation at 1206, 1141, 1070, and 880 cm^{−1}. In addition, appearance of bands from 900 to 650 cm^{−1} can indicate an increase in aromatic nature for the activated compounds. The presence of large quantities of phosphorous on the surface of phosphoric acid activated carbons has been confirmed with energy-dispersive X-ray spectrometry (Dastgheib and Rockstraw, 2001). While the type of phosphorous groups present on the surface was not determined in our studies, Benaddi et al. (2000) postulated, based on measured surface acidity constants, that phosphonic acids, phosphonous acids, and phosphines were likely functional groups in phosphoric acid-activated carbons made from wood.

The FTIR results strongly support significant spectral and chemical changes occurring with the activation of the pecan shells with phosphoric acid and heat treatment. As noted earlier, these changes are observed even at the low oxygen levels (e.g., 4% O₂ at 100 mL/min of air). There are only minor spectral differences in the 100 mL/min (4.0% O₂) and 400 mL/min (7.6% O₂) spectra from 1650 cm^{−1} to 700 cm^{−1}, but the spectral changes attributed to the formation of phosphorous containing groups increased steadily and significantly thereafter, as shown in Fig. 4. This would suggest that, oxygen level during activation is important if the formation of phosphorous-containing groups on the activated carbon's surface is desired.

3.3. Activated carbon surface area and yields

The specific surface areas of the laboratory-manufactured activated carbons ranged from 864 to 915 m²/g (Table 1). While the greatest surface area was noted for activated carbon obtained with the highest levels of oxygen, there was no observable trend which was dependent on the oxidative conditions. Likewise, the micropore volume was not influenced by the oxidative conditions. These findings correspond well with those presented by Molina-Sabio et al. (1995a), who found that the atmosphere (nitrogen or air) did not affect the pore structure when sufficient phosphoric acid was used in the impregnation. Other studies have shown that concentration of phosphoric acid, activation temperature, and impregnation conditions are mainly responsible for creating the physical pore structure (Jagtoyen and Derbyshire, 1993; Molina-Sabio et al., 1995b). Thus we conclude that the various atmospheres used in our studies were mainly responsible for surface chemistry changes but not for pore structure. The specific surface area and micropore volume were lower than that of the commercial phosphoric acid activated carbon, but the values obtained by the

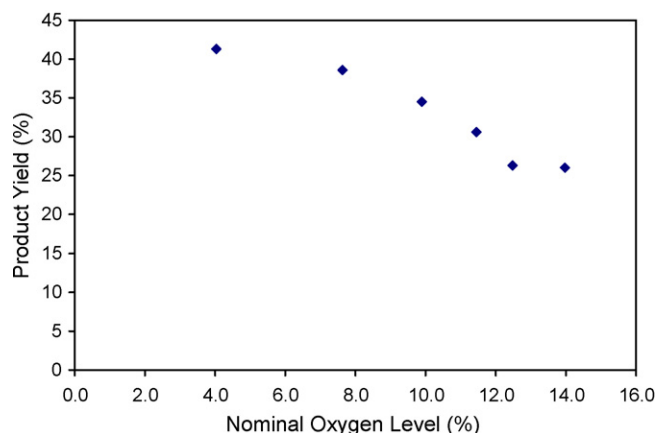


Fig. 5. Product yield of laboratory-manufactured activated carbon made from phosphoric acid impregnated pecan shells.

experimental carbons compare well with recent studies (Guo and Rockstraw, 2007). The washed activated carbons resulted in overall product yields of 26–41% (Fig. 5); higher yields were obtained when the air flow through the furnace was lower and the oxygen level was less. These yields are similar to those obtained by Toles et al. (1998) for pecan shells activated with a higher concentration of phosphoric acid and a slightly different activation method, and they were significantly higher than the yield of 18%, which was obtained through steam activation of pecan shell-based activated carbon (Ng et al., 2003). The finding that yield and specific surface area were not related during the phosphoric acid activation is in contrast with that found in the case of steam activation. In steam activation, a linear relationship has been found between yield and specific surface area (Johns et al., 1999).

3.4. Activated carbon performance

The ability of the activated carbons to adsorb copper ions was dependent on the oxygen level in the furnace, and the resulting adsorptive capacity of the activated carbons made with the highest oxygen levels was almost double that of the carbon activated with the lowest oxygen levels (Fig. 6). In both studies (with 10 and 20 mM of Cu^{2+}), the relationship between oxygen level during activation and adsorptive capacity appeared almost linear in the range of oxygen levels studied. In the best case, the adsorption of cop-

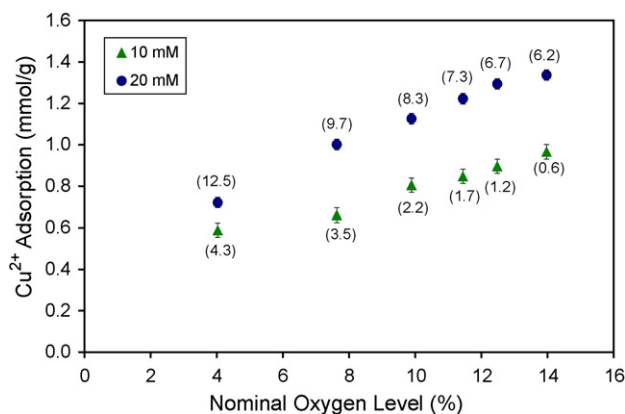


Fig. 6. Copper(II) adsorption from aqueous medium for activated carbons made at different oxygen levels. Error bars reflect one standard deviation calculated using technique based on duplicate measurements (Taylor, 1990). Values in parenthesis correspond to final copper(II) equilibrium concentrations. Norit C adsorbed 0.26–0.27 mmol/g of carbon (at 10 and 20 mM starting concentrations) in control experiments (data not shown in figure).

per(II) was 0.97 and 1.3 mmol/g of carbon after contact with 10 mM and 20 mM of Cu^{2+} , respectively (Fig. 6). This compared favorably with the results obtained by Toles et al. (1998), who found that capacities ranged from 0.23 to 0.86 mmol/g for phosphoric acid (50%) activated pecan shells, when using a variety of different activation strategies (other than the one studied here). The adsorption capacity was about 10–13% lower than determined by Lima et al. (2004) and Marshall et al. (2007) when using the same activation method for hardwood and flax shive, but it was significantly higher than Norit C (Fig. 6) and several other commercial carbon products when tested under the same conditions (Lima et al., 2004; Marshall et al., 2007). While the current studies only involved copper cation adsorption, previous studies have shown that the phosphoric acid activation is also suitable for adsorption of other metals such as lead, nickel, and zinc (Bansode et al., 2003; Marshall et al., 2007).

4. Conclusions

The results have shown that the oxygen level present during activation of phosphoric acid-impregnated pecan shells is an important factor when activated carbon is tailor-made for aqueous copper(II) cation adsorption. More active surface groups, of the type responsible for attracting positive, ions were found in carbons prepared in a more oxidizing atmosphere. These groups contributed to the high levels of Cu^{2+} adsorption. In addition, the results showed that more phosphorous was incorporated into the surface in an oxidizing atmosphere. The level of oxidation correlated well surface charge and was a strong indicator of copper uptake ability. The surface area of the activated carbon was much less dependent on the oxidizing atmosphere and only varied with 3% around the mean, which was in agreement with previous studies.

Acknowledgements

The authors would like to thank Bruker Optics for assisting with the FTIR data collection. The mention and use of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

References

- Bansode, R.R., Losso, J.N., Marshall, W.E., Rao, R.M., Portier, R.J., 2003. Adsorption of metal ions by pecan shell-based granular activated carbons. *Bioresour. Technol.* 89, 115–119.
- Benaddi, H., Bandoz, T.J., Jagiello, J., Schwartz, J.A., Rouzaud, J.N., Legras, D., Béguin, F., 2000. Surface functionality and porosity of activated carbons obtain from chemical activation of wood. *Carbon* 38 (5), 660–674.
- Bevia, F.R., Rico, D.P., Gomis, A.F.M., 1984. Activated carbons from almond shells. Chemical activation. 1. Activating reagent selection and variables influence. *Ind. Eng. Chem. Prod. Res. Dev.* 23, 266–269.
- Dastgheib, S.A., Rockstraw, D.A., 2001. Pecan shell activated carbon: synthesis, characterization, and application for the removal of copper from aqueous solution. *Carbon* 39 (12), 1849–1855.
- Guo, Y., Rockstraw, D., 2007. Physicochemical properties of carbons prepared from pecan shells by phosphoric acid activation. *Bioresour. Technol.* 98 (8), 1513–1521.
- Jagtøyen, M., Derbyshire, F., 1993. Some considerations of the origins of porosity in carbons from chemically activated wood. *Carbon* 31 (7), 1185–1192.
- Jagtøyen, M., Thwaites, M., Stencil, J., McEnaney, B., Derbyshire, F., 1992. Adsorbent carbon synthesis from coals by phosphoric acid activation. *Carbon* 30 (7), 1089–1096.
- Johns, M.M., Marshall, W.E., Toles, C.A., 1999. The effect of activation method on the properties of pecan shell-activated carbon. *J. Chem. Technol. Biotechnol.* 74, 1037–1044.
- Lima, I.M., Marshall, W.E., Wartelle, L.H., 2004. Hardwood-based granular activated carbons for metals remediation. *J. AWWA* 96 (7), 95–102.
- Marshall, W.E., Wartelle, L.H., Akin, D.E., 2007. Flax shive as a source of activated carbon for metals remediation. *Bioresources* 2 (1), 82–90.
- Molina-Sabio, M., Caturla, F., Rodríguez-Reinoso, F., 1995a. Influence of the atmosphere used in the carbonization of phosphoric acid impregnated peach stones. *Carbon* 33 (8), 1180–1182.
- Molina-Sabio, M., Rodríguez-Reinoso, F., Caturla, F., Selles, M.J., 1995b. Porosity in granular carbons activated with phosphoric acid. *Carbon* 33 (8), 1105–1113.

- Ng, C., Marshall, W.E., Rao, R.M., Bansode, R.R., Lasso, J.N., Portier, R.J., 2003. Granular Activated Carbons from Agricultural By-products: Process Description and Estimated Cost of Production. Bulletin Number 881. Louisiana State University AgCenter, Baton Rouge, LA.
- NASS, 2007. Noncitrus Fruits and Nuts, July 2007. U.S. Department of Agriculture, National Agricultural Statistical Service, pp. 3 and 72–74.
- Solum, M., Pugmire, R., Jagtoyen, M., Derbyshire, F., 1995. Evolution of carbon structure in chemically activated wood. *Carbon* 33 (9), 1247–1254.
- Taylor, J.K., 1990. *Statistical Techniques for Data Analysis*. Lewis Publishers, Chelsea, MI.
- Toles, C.A., Marshall, W.E., Johns, M.M., 1998. Phosphoric acid activation of nutshells for metals and organic remediation: process optimization. *J. Chem. Technol. Biotechnol.* 72, 255–263.
- Toles, C.A., Marshall, W.E., Johns, M.M., 1999. Surface functional groups on acid-activated nutshell carbons. *Carbon* 37 (8), 1207–1214.
- Toles C.A., Marshall, W.E., Johns, M.M., 2000a. Activated nutshell carbons from agricultural waste. U.S. Patent 6,033,573.
- Toles, C.A., Marshall, W.E., Johns, M.M., Wartelle, L.H., McAloon, A., 2000b. Acid-activated carbons from almond shells: physical, chemical and adsorptive properties and estimated cost of production. *Bioresour. Technol.* 71, 87–92.
- USDOE, 2005. Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply, DOE/GO-102995-2135. U.S. Department of Energy, Office of Scientific and Technical Information, Oak Ridge, TN, pp. 5–33.
- Wartelle, L.H., Marshall, W.E., 2001. Nutshells as granular activated carbons: physical, chemical and adsorptive properties. *J. Chem. Technol. Biotechnol.* 76, 451–455.
- Whitehead, T.H., Warshaw, H., December 1938. Studies in the Utilization of Georgia Pecans, vol. 1, no. 5. State Engineering Experimental Station Bulletin, The Georgia School of Technology.